

Charge Density Studies of Mixed Valence Trinuclear Oxo-Bridged Iron Complexes

J. Overgaard, B.B. Iversen and F.K. Larsen (U. of Aarhus, Denmark)

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Beamline(s): X3A1

The multi-temperature study of the trinuclear oxo-bridged mixed valence iron complex, $[\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CH}_3)_3)_6(\text{NC}_5\text{H}_5)_3]$, which was previously carried out at beamline X3 (Wilson et al, in press), showed that the electron transfer process in this complex only involves two of the three iron sites and at temperatures below 30 K the trinuclear iron core seems to be completely valence trapped. We have now carried out a charge density study for this compound based on 130460 reflections collected with the CCD SMART area detector at beamline X3A1 with the crystal cooled to 28 K. The 32582 unique reflections, which has an internal agreement of 3.4%, were used in the subsequent modeling of the electron density distribution with program XD. Unexpectedly the central oxygen atom, which has an approximate trigonal coordination to the iron atoms, nevertheless shows a sp^3 -like hybridisation. This also points to fundamentally different interactions with the two formally identical Fe^{III} sites, conforming with the fact that only one of the Fe^{III} sites is valence trapped at all temperatures. The figure shows the model deformation map of the trinuclear core.

The trinuclear iron chloroacetate complex, $[\text{Fe}_3\text{O}(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$, is another mixed-valence compound, which valence traps by lowering the temperature. In fact it is known from Mossbauer spectra taken at various temperatures that two distinct states, Fe^{IIA} and Fe^{IIB} , exist at low temperatures, and that valence delocalization takes place between only two iron atoms, Fe^{IIA} and Fe^{II} , with increasing temperature (Sato et al 1996).

We have continued our studies of the mixed valence trinuclear oxo-bridged complexes by a low-temperature study of, $[\text{Fe}_3\text{O}(\text{CH}_2\text{ClCOO})_6(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$, using the CCD SMART area detector and cooling the crystal by the newly developed cryostat which allows to collect data with the crystal cooled to about 20 K by a stream of cold He gas. The modeling based on these data is still in progress, and features in the density distribution of the trinuclear core including the sp^3 -like hybridisation of the μ^3 -oxygen atom and differences in the Fe^{II} - μ^3 -oxygen bonds are observed also in this complex.

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References: C. Wilson, B.B. Iversen, J. Overgaard, F.K. Larsen, G. Wu, S.P. Palii, G.A. Timco, N.V. Gerbelevu, *J. Am. Chem. Soc.*, in press. T. Sato, F. Ambe, K. Endo, M. Katada, H. Maeda, T. Nakamoto, H. Sano, *J. Am. Chem. Soc.* 118, 3450, 1996.

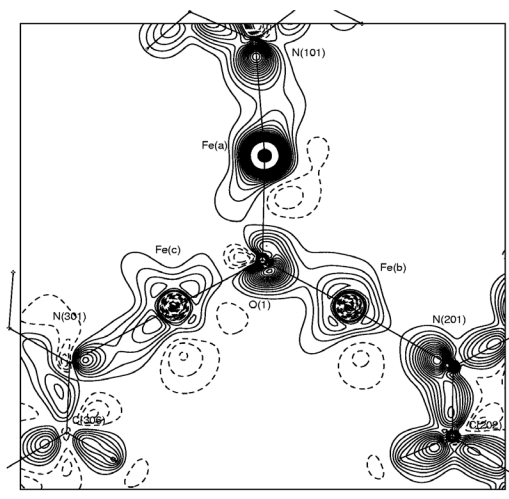


Figure 1 Static deformation map in the plane of the two Fe^{III} and one Fe^{II} site of the $\text{Fe}_3\text{O}(\text{pivalate})_6(\text{pyridine})_3$ complex. 0.1 $\text{e}/\text{\AA}^3$ between contour levels.